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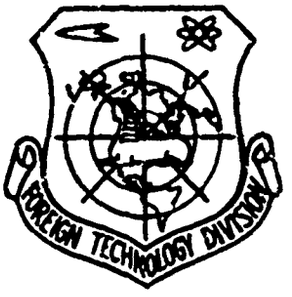
THERMAL EXPANSION OF THE SOLID SOLUTIONS OF REFRACTORY METALS IN GROUPS IV, V, AND VI OF THE PERIODIC SYSTEM

by

K. S. Pridantseva and N. A. Solov'yeva



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As a result of studying the thermal expansion of the solid solutions of refractory metals in groups IV, V and VI of the periodic system it has been established that in the curves of the dependence of the coefficient of thermal expansion upon composition in all the investigated solid solutions, no minima or maxima inherent in alloys with a ferromagnetic anomaly or in the alloys in which phases of the delta-phase are formed have been detected. In all cases the coefficient of thermal expansion of the single-phase solid solutions of refractory metals has either an approximately linear dependence upon composition (chromium-vanadium, chromium-molybdenum, molybdenum-niobium, zirconium-titanium), or changes on a curve, while remaining in magnitude within the limits of the values of the coefficients of thermal expansion for the elements forming the system (molybdenum-vanadium, niobium-vanadium).

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By: K. S. Prodantseva and N. A. Solov'yeva

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Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
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Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
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М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

THERMAL EXPANSION OF THE SOLID SOLUTIONS OF REFRACTORY METALS IN GROUPS IV, V AND VI OF THE PERIODIC SYSTEM

K. S. Pridantseva and N. A. Solov'yeva

(Moscow)

Today, for various vacuum junctions with dielectrics (glass, ceramics, mica, sapphire and others) ferromagnetic alloys with an anomaly of thermal expansion are widely used; they have relatively low coefficients of thermal expansion which are close in value to the indicated dielectric materials. However; the low coefficients of expansion of these alloys are maintained only up to the magnetic transition temperature, i.e., to 400-500°C. With a rise in the temperature coefficient of thermal expansion for ferromagnetic alloys sharply increases while the temperature coefficient of thermal expansion of a number of dielectric materials is changed very little with temperature.

Despite numerous studies of both a theoretical and an experimental nature, up to now efforts to obtain ferromagnetic alloys with a low coefficient of thermal expansion at temperatures above 450°C have been unsuccessful. In connection with this,

a new direction was selected – investigating alloys based on refractory metals, which, as a rule, have low coefficients of thermal expansion over a wide range of temperatures.

The general adherences to the law of thermal expansion were investigated for the single-phase solid solutions of certain binary systems of refractory metals in groups IV, V and VI of the periodic system: molybdenum-chromium, molybdenum-niobium, molybdenum-vanadium, chromium-vanadium, niobium-vanadium, zirconium-titanium, zirconium-hafnium, and also for comparison chromium-iron and vanadium-iron. In the last two binary systems, dependence of the coefficient of expansion upon the composition in both the ferromagnetic and in the paramagnetic ranges was revealed.

Alloys were prepared by the cermet method (in the first stage of the investigations) and also by the method of arc smelting pure burden materials. Alloys of the zirconium-titanium and zirconium-hafnium systems were made from iodide materials. Alloys of the chromium-vanadium, chromium-iron and vanadium-iron systems were smelted in an induction furnace in argon.

The thermal expansion of the alloys was studied in cast and cermet specimens, which were preliminarily homogenized at temperatures which ensure the equilibrium state of the alloys. Homogenizing annealing was done in a vacuum no less than 10^{-4} mm Hg or in argon.

For dilatometric research on the majority of the alloys, a quartz dilatometer made by Professor P. G. Strelkov was used. This instrument, which in sensitivity ($2.2 \cdot 10^{-5}$ mm/div) approaches the classical interference dilatometer, is intended especially for studying the small specimens. Measurements were made by the

absolute method to 800-900°C in vacuum. The measurement error does not exceed 1%. Some cermet specimens of the alloys smelted in the induction furnace were measured on an indicator dilatometer. The measuring error on this instrument comprised 2-3%.

The results of research on the thermal expansion of solid solutions are presented in the form of graphs of the dependence of the average coefficient of thermal expansion upon composition.

Figure 1 shows the variation of the coefficient of expansion with composition for alloys of the chromium-molybdenum system (the cermet specimens) in three temperature ranges - 20-300, 20-500 and 20-700°C. It is evident that the coefficient of expansion of chromium-base solid solutions monotonically decreases with an increase in their molybdenum content.

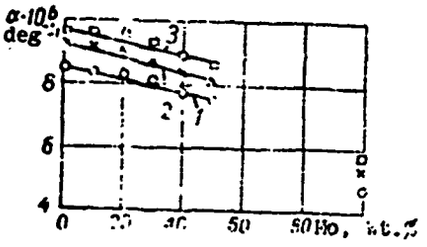

Fig. 1. The variation in the coefficient of thermal expansion for alloys of the chromium-molybdenum system in the temperature ranges 20-300 (1), 20-500 (2) and 20-700°C (3) as a function of composition.

In the chromium-vanadium system an extremely flat shape of the expansion curves is observed in the same temperature ranges. The coefficient of thermal expansion of the solid solutions of this system varies almost linearly with composition between the values of the coefficients of expansion of pure metals - chromium and vanadium; this is illustrated by Fig. 2.

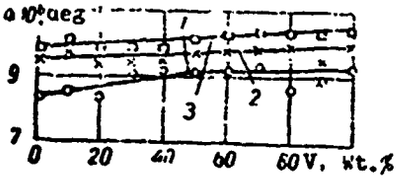

Fig. 2. The variation in the coefficient of thermal expansion for the solid solutions of the chromium-vanadium system in the temperature ranges 20-300 (1), 20-500 (2) and 20-700°C (3) as a function of composition (annealing at 1000°C for 24 h).

In the niobium-vanadium system the coefficient of thermal expansion of solid niobium-base solutions increases linearly with composition up to a 50 wt. % vanadium content. With a further increase in the vanadium content in solid solutions with niobium, the coefficient of expansion of the alloys is barely changed and in terms of values approaches the coefficient of expansion of pure vanadium. The concentration dependence, which is characterized by the variation in the shape of the expansion curves for the solid solutions of this system in the 20-300 and 20-900°C temperature ranges, is shown in Fig. 3.

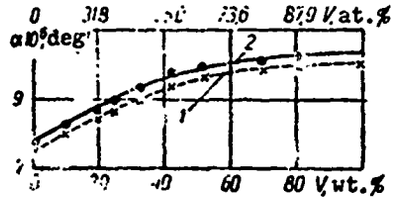

Fig. 3. The variation in the coefficient of thermal expansion with the composition of solid solutions in the niobium-vanadium system in the 20-300 (1) and 20-900°C (2) temperature ranges.

The variation with composition of the coefficient of thermal expansion for the solid solutions of the molybdenum-niobium, molybdenum-vanadium and molybdenum-chromium systems in the 20-800°C range is presented in Fig. 4. For comparison, this graph gives V. N. Yeremenko's findings for the same temperature range, which he obtained in cermet alloys of the molybdenum-niobium system [1].

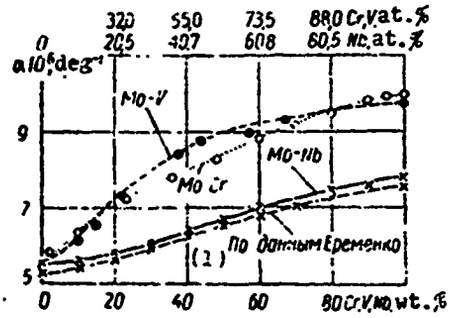

Fig. 4. The influence of the second element content on the coefficient of thermal expansion of solid solutions with molybdenum in the 20-800°C range.

KEY: (1) According to the findings of Yeremenko.

As can be seen from Fig. 4, with an increase in the second element content in solid solutions containing molybdenum, the coefficient of thermal expansion increases, but with different degree of deviation from additivity. An almost linear dependence of the coefficient of thermal expansion upon composition is observed in the solid solutions of the molybdenum-niobium system, and a noticeable deviation from linearity is observed in solid solutions of molybdenum-vanadium and molybdenum-chromium. The addition of both chromium and vanadium sharply increases the coefficient of thermal expansion of molybdenum. The influence of vanadium on the increase in the coefficient of thermal expansion is especially noticeable with a content of up to 40-50% vanadium in solid solutions containing molybdenum. With a further increase in vanadium concentration, its effect is small, which is analogous to the influence which vanadium exerts on the variation in the coefficient of thermal expansion for the solid solutions in the niobium-vanadium system (see Fig. 3). However, the variation in the slope of the concentration curves of thermal expansion for the solid solutions of the niobium-vanadium and molybdenum-vanadium systems shows that the values of the coefficients of thermal expansion of all solid solutions do not go beyond the limits of the value of the coefficient of thermal expansion for pure vanadium, just as the value of the coefficients of thermal expansion for the solid solutions of the molybdenum-chromium system do not exceed the values of this parameter for pure chromium.

Figure 5 gives a graph of the concentration dependence of the thermal expansion of the solid solutions of the zirconium-titanium system in the 20-500°C range (cast specimens). Here the influence of an admixture of hafnium in the initial zirconium on the indicated composition-property dependence has been shown.

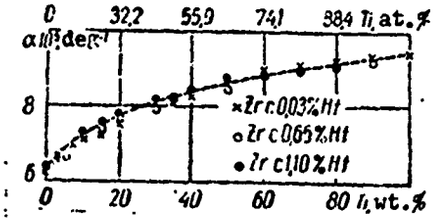

Fig. 5. The concentration dependence of the coefficient of thermal expansion of alloys of the zirconium-titanium system and the influence of an admixture of hafnium on this dependence in the 20-500°C range.

Figure 6 illustrates the variation with composition of the coefficient of thermal expansion of the solid solutions of the same system, depending on state and means of making the alloys: by casting (1), by deformation (2) and by cermet methods (3), in the 20-200°C range.

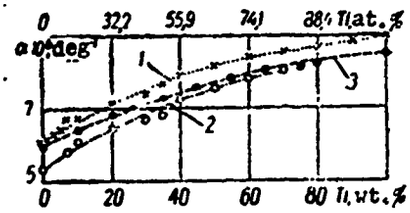

Fig. 6. The variation with composition of the coefficient of thermal expansion of solid solutions in the zirconium-titanium system, depending on state and means of obtaining alloys, in the 20-200°C range.

From the graphs presented in Figs. 5 and 6, it is apparent that the coefficient of thermal expansion of the solid solutions of the zirconium-titanium system changes continuously with little deviation from additivity – from the values of the coefficient of thermal expansion of pure zirconium to the values of the coefficient of expansion of cast and cermet titanium. It is also evident that the influence of an admixture of hafnium in the initial zirconium (0.03-0.65 and 1.1 weight % hafnium) on the coefficient of thermal expansion of its solid solutions containing titanium is insignificant. The thermal expansion curve of the deformed specimens is somewhat below and almost parallel to the thermal expansion curve of the cast specimens (see Fig. 6).

This difference in the thermal expansion between the cast and deformed specimens was observed also in individual zirconium-base alloys, especially in an alloy containing 10% halfnium, which

was reported in work [4]. Such a phenomenon is explained by the preferred orientation which takes place in metals with an hexagonal structure after cold deformation.

The lower values of the coefficients of thermal expansion of the cermet specimens in comparison with the case specimens of alloys of approximately the same compositions are apparently explained by their contamination by impurities, mainly by oxygen, whose content in the cermet specimens reached 1%. One ought to add that this phenomenon is not connected with a change in the density of cermet specimens when heating them in measurements up to 900°C, since their length before and after testing remained identical. The data given in Fig. 4 show that even in the molybdenum-niobium system in the cermet specimens of the alloys lower values of the coefficient of thermal expansion were also obtained in comparison with the cast specimens.

The experimental findings given in Fig. 7 show that in the iron-chromium system the coefficient of thermal expansion of magnetic iron-base solutions even with a solution in them of 5% chromium sharply decreases from $13 \cdot 10^{-6}$ deg^{-1} for pure iron to $11.8 \cdot 10^{-6}$ deg^{-1} in the alloy in the 20-300°C temperature range. With a further increase in the chromium content in iron to 30%, the slope of the thermal expansion curves becomes less steep; at 40% chromium the coefficient of thermal expansion barely changes in the 20-300, 20-500 and 20-700°C temperature ranges, but at 45% chromium the coefficient of thermal expansion of the nonmagnetic alloy increases intermittently. At a 50% content of chromium in the iron-chromium system the coefficient of thermal expansion also drops sharply, and with a further increase in chromium content it monotonically decreases both in the magnetic and paramagnetic domains of this system.

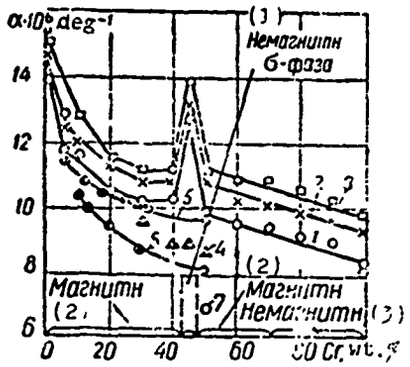

Fig. 7. The variation in the coefficient of thermal expansion of alloys of the iron-chromium system, depending on composition and structure in the 20-300, 20-500 and 20-700°C temperature ranges: 1 — 20-300°C, treatment at 710°C for 240 h; 2 — 20-500°C, treatment at 710°C for 240 h; 3 — 20-700°C, treatment at 710°C for 240 h; 4 — 20-300°C, hardening from 1000°C; 5 — 0-250°C [7]; 6 — 20-300°C, annealing at 950°C [2]; 7 — 20-100°C, annealing at 950°C [2].

KEY: (1) Nonmagnetic, σ-phase; (2) Magnetic; (3) Nonmagnetic.

The concentration dependence of the coefficient of thermal expansion in the iron-chromium system was investigated in alloys subjected to prolonged homogenizing annealing at 710°C for 240 h, which ensures the equilibrium state of the alloys and the formation of σ-phase at the appropriate compositions. Therefore, the peak on the composition property diagram corresponds to the presence of a uniform nonmagnetic σ-phase with a new crystalline structure and with lattice parameters ($a = 8.800$ Å and $c = 4.544$ Å) which differ sharply from the values of the lattice parameters of pure metals — iron and chromium which form the system. The presence of a uniform σ-phase in an alloy with 45 weight % chromium was confirmed by radiographic and microscopic analyses. It was established also that after hardening of this alloy from a temperature of 1000°C (higher than the stability of the σ-phase), it again acquires magnetic properties and its coefficient of thermal expansion decreases very sharply, which is clearly evident from the graph in Fig. 7. Data on the thermal expansion of certain alloys based on the iron-chromium system containing up to 50% chromium have been entered here. The data were obtained in work [5], in which the σ-phased alloys were not studied.

Approximately the same behavior pattern of the coefficient of thermal expansion in dependence on composition is observed

also in the iron-vanadium system, in which the σ-phase is formed in the content range of about 50 weight % vanadium after prolonged annealing at a temperature of 1000°C.

As a result of studying the thermal expansion of the solid solutions of refractory metals in groups IV, V and VI of the periodic system it has been established that in the curves of the dependence of the coefficient of thermal expansion upon composition in all the investigated solid solutions, no minima or maxima inherent in alloys with a ferromagnetic anomaly or in the alloys in which phases of the σ-phase are formed have been detected.

In all cases the coefficient of thermal expansion of the single-phase solid solutions of refractory metals has either an approximately linear dependence upon composition (chromium-vanadium, chromium-molybdenum, molybdenum-niobium, zirconium-titanium), or changes on a curve, while remaining in magnitude within the limits of the values of the coefficients of thermal expansion for the elements forming the system (molybdenum-vanadium, niobium-vanadium).

The obtained experimental findings made it possible to find among the investigated systems of refractory metals adequate bases and compositions of nonmagnetic alloys with low (assigned) coefficients of thermal expansion and satisfactory plasticity for the manufacture of airtight junctions with dielectrics. The results of testing the developed alloys in junctions with ceramics have been published in works [2, 3].

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